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Electrochemical studies on organometallic compounds

XVIII *. Electroreduction of dichloro(5,10,15,20-tetra-*p*-tolylporphyrinato)vanadium(IV)

P. Reeb and Y. Mugnier

Laboratoire de Synthèse et d'Electrosynthèse Organométalliques associé au CNRS (UA 33), Faculté des Sciences, 6 bd Gabriel 21000 Dijon (France)

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Abstract

In tetrahydrofuran (thf) at −30 °C, the compound $V^{IV}LX_2$ (**1**: L = 5,10,15,20-tetra-*p*-tolylporphyrinate(2 −); X = Cl) is reduced in two monoelectronic steps to give respectively the monoanion $V^{III}LX_2^-$ (**2**) and the dianion $V^{II}LX_2^{2-}$ (**3**). The species $V^{III}LX_2^-$ slowly reacts with the solvent, yielding $V^{III}LX(thf)$ (**5**), which has been isolated. Electrochemical reduction of **5**, or slow chemical transformation of **3** gives $V^{II}LS_2$ (**6**). The various reactions are discussed in detail in terms of square schemes.

Introduction

The vanadium(II) porphyrins $V^{II}L(PPhMe_2)_2$ and $V^{II}L(thf)_2$ (L = porphyrin macrocycle; thf = tetrahydrofuran) have been prepared recently [1,2] by chemical reduction of the dihalogenovanadium(IV) porphyrins $V^{IV}LX_2$ (X = Cl or Br); the V^{III} complexes were not obtained. It had previously been predicted from theoretical studies [3] that the V^{II} should be more stable than the V^{III} complexes.

In a preliminary communication [4], we described the first V^{III} porphyrin $V^{III}LClS$ (S = thf) obtained by electroreduction of $V^{IV}LCl_2$. In this paper, we present the general mechanism for the electrochemical reduction of these compounds.

Results

At room temperature in THF, $V^{IV}LX_2$ decomposes rapidly; initially, several waves are observed, with heights which vary with time. In contrast at low tempera-

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* Part XVII, see ref. 4.

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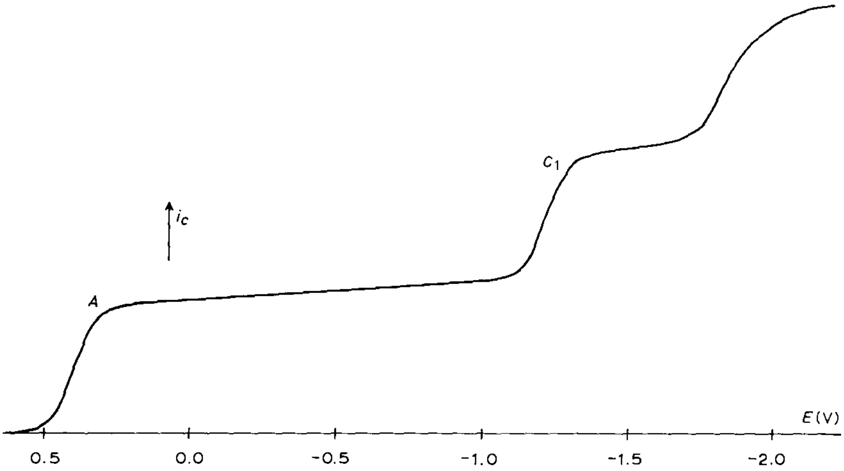

Fig. 1. R.d.e. voltammogram at −30 °C of $V^{IV}LX_2$ in thf.

ture (−30 °C) **1** is stable, and two-well defined waves *A* and C_1 appear on the r.d.e. voltammogram * (Fig. 1). On a stationary electrode, the two corresponding peaks *A* and C_1 are observed, but additional peaks *B* and C_2 appears (Fig. 2); the height of *B* decreases when the temperature is lowered from −30 °C to −60 °C.

Five oxidation peaks C'_2, C'_1, B', B'_1 and A' are observed by cyclic voltammetry when the scan is reversed after peak C_2 (Fig. 3). Peak A' corresponds to the oxidation of the species formed by reduction along peak *A*, and peaks B' and B'_1 to that of the species formed along peak *B* (Fig. 3).

After exhaustive electrolysis of **1** on a Pt electrode at −30 °C at 0 V (wave *A*), 0.53 F are consumed and a brown solution is obtained. The stationary voltammogram of this solution exhibits three reduction peaks A_α, *B*, and C_2 (Fig. 4).

If the electrolysis is carried on at the potential of peak A_α (−0.8 V), 0.48 F are again consumed and the r.d.e. voltammogram shows the two waves *B* and C_2 (Fig. 5a). The cyclic voltammogram of the solution is shown in Fig. 5b; the relative height of peaks B' and B'_1 depend on the temperature and on the sweep-rate. B'_1 decreases when the temperature is lowered from −30 °C to −60 °C and when the

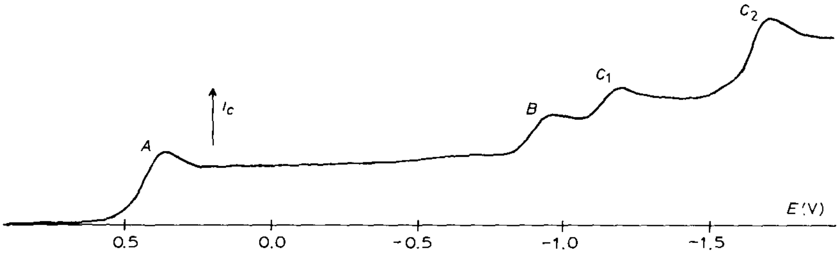

Fig. 2. Voltammogram at −30 °C of $V^{IV}LX_2$ in thf on a stationary electrode.

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* Another wave appears at more negative potentials in all the cases we describe, this wave corresponds to the reduction of the macrocycle, and is not discussed here.

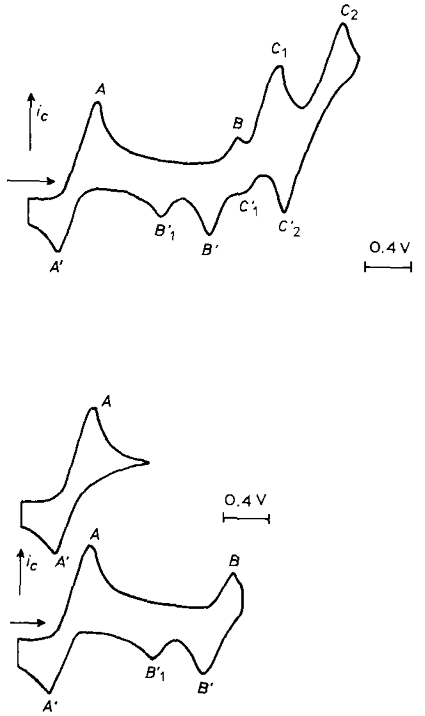


Fig. 3. Cyclic voltammogram at −30 ° C of $V^{IV}LX_2$ in thf. Starting potential: +0.8 V; sweep rate 200 mV s^{-1}.

sweep rate is increased. The height of B' increases relative to that of B'_1 upon addition of chloride ions (LiCl in thf).

The same results are obtained, with consumption of 1 F, when the electrolysis of **1** is carried out directly at the potential of peak A_α (−0.8 V). When the electrolysis

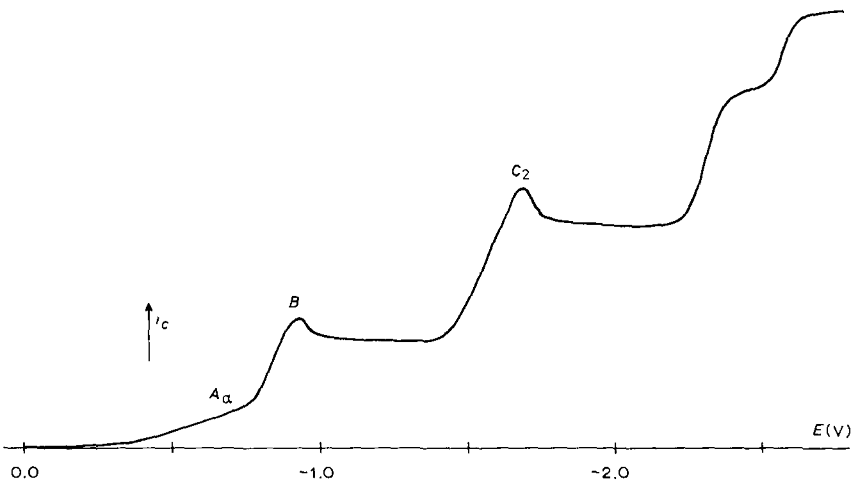


Fig. 4. Voltammogram on stationary electrode at −30 ° C after reduction of $V^{IV}LX_2$ at 0 V.

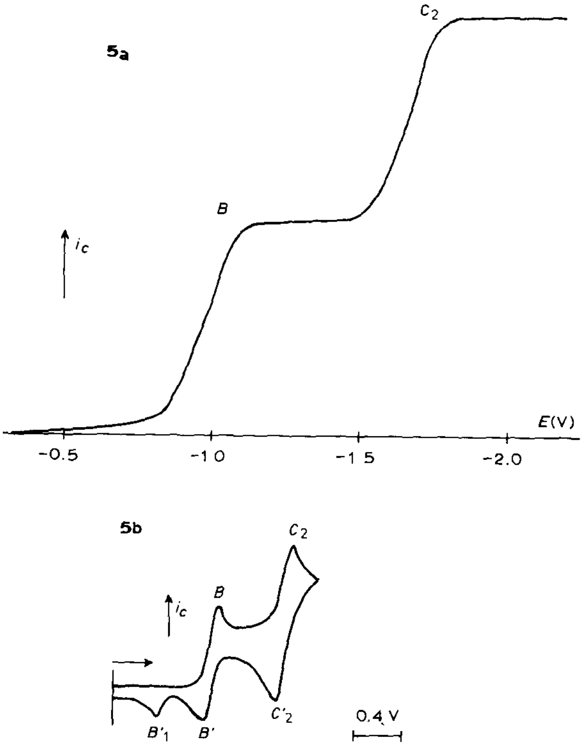


Fig. 5. (a) R.d.e. voltammogram at −30 °C after reduction of $V^{IV}LX_2$ at −0.8 V; (b) cyclic voltammogram at −30 °C after reduction of $V^{IV}LX_2$ at −0.8 V. Starting potential: 0 V; sweep rate 100 mV s^{-1}.

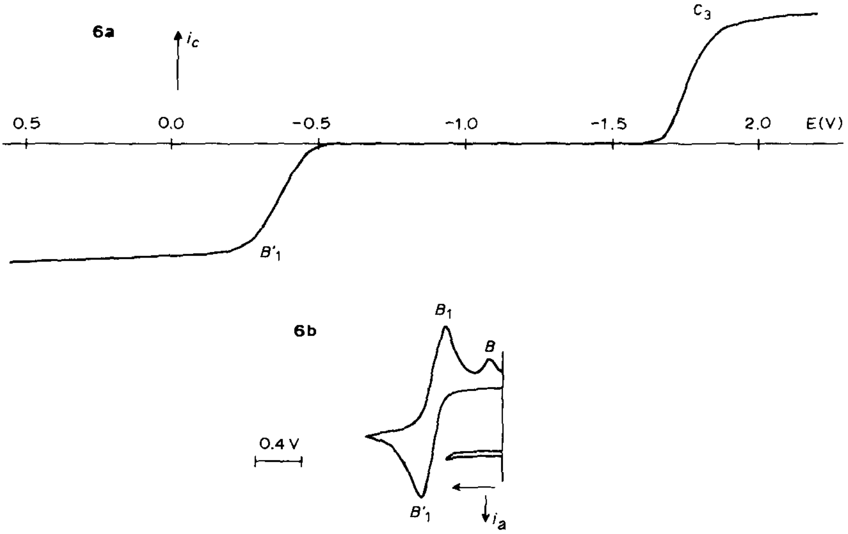


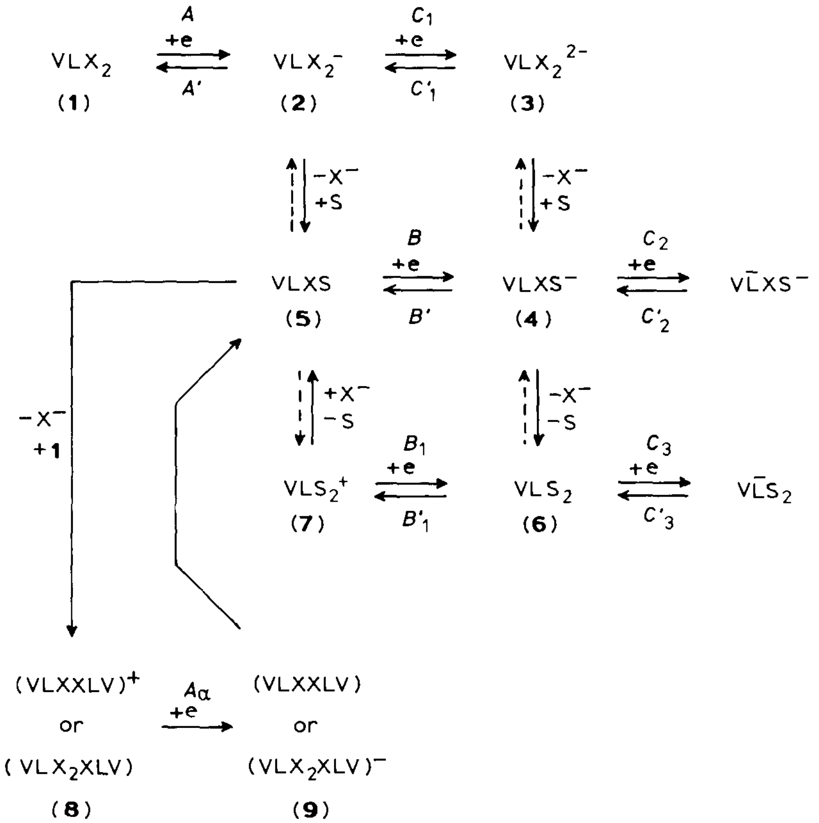
Fig. 6. (a) R.d.e. voltammogram at −30 °C after reduction of $V^{IV}LX_2$ at −1 V; (b) cyclic voltammogram at −30 °C after reduction of $V^{IV}LX_2$ at −1 V. Starting potential: −1 V; sweep rate 100 mV s^{-1}.

solution is electrolyzed at the potential of wave B (-1 V), 1 F is consumed and a deep blue solution is formed. (Electrolysis of **1** at -1 V gives the same solution with consumption of 2 F). The solution obtained shows the same spectroscopic and electrochemical characteristics as an authentic sample of $V^{II}LS_2$ prepared by convential procedures [2]. The r.d.e. voltammogram of this solution consists of one reduction wave C_3 and one oxidation wave B'_1 (Fig. 6a). The cyclic voltammogram shows peaks B'_1, B and a new peak B_1 which forms a reversible system with B'_1 (Fig. 6b). A decrease in the sweep rate causes an increase of B relative to B_1.

Discussion

Reduction of 1

The differences observed when methods with different time-scales are used show that chemical reactions accompany the electrochemical reactions. The results can be rationalized in terms of Scheme 1.



L = 5,10,15,20-tetra-*p*-tolylporphyrinate (−2)

S = thf

X = Cl

Scheme 1

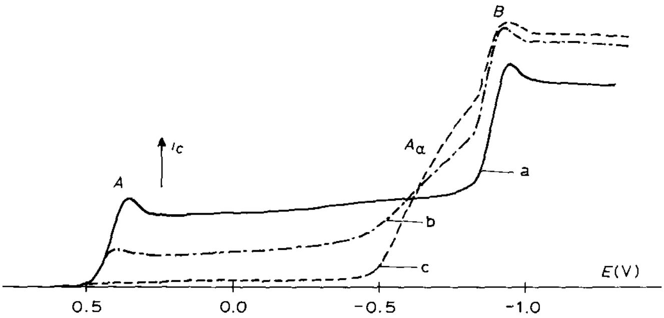


Fig. 7. Voltammogram at −30 °C of equimolar quantities of $V^{III}LXS$ (5) and $V^{IV}LX_2$; t (min): (a) 0, (b) 90, (c) 240.

On the time-scale of the r.d.e. voltammetry, the chemical reactions are too slow to have an effect, and two successive 1e reductions occur (waves A and C_1, Fig. 1). These processes are reversible, as shown by the cyclic voltammetry couples of peaks A/A' and C_1/C_1' (Fig. 3).

In cyclic voltammetry at slow sweep rates, there is enough time for **2** to lose one Cl^- to give **5**, which is reversibly reduced along peak B (Fig. 3). We have isolated **5** by controlled potential electrolysis (see Experimental section); it does indeed, give peak B. This mechanism is also confirmed by a study of the behaviour of **6** (square scheme **6**, **4**, **5**, **7**; vide infra).

A slower chemical reaction takes place on the time scale of controlled potential electrolysis. When **1** is reduced at 0 V, only 0.5 F are involved, and the product obtained is again reducible with consumption of 0.5 F (wave A_α) to give **5**; this shows that the product of the reduction, **5**, reacts with **1** to give a dimeric compound **8**, which is reduced along wave A_α, whose probable structure is shown in Scheme 1. The vanadium atoms are probably linked by chlorine bridges; the existence of both types of structure has been demonstrated in the case of other metals bound to cyclopentadienyl rings [5]. Compound **5** slowly reacts chemically with **1**; wave A disappears and wave A_α appears during the reaction (Fig. 7). The reduction of **8** to **5** probably takes place via the intermediate compound **9**. We tried to isolate **8**, but did not succeed because of its instability at room temperature.

Reduction of 5 and oxidation of 6 (square scheme 5, 4, 6, 7)

As mentioned earlier, we isolated **5**, and studied its voltammetric behaviour (Fig. 5). The height of peak B' increases relatively when the sweep rate is increased or the temperature decreased, whereas that of B'_1 decreases. These voltammograms are typical of a "square scheme" [6,7] reaction, in which the reaction **4** → **6** is slow, so that, when the scan is reversed, **4** gives **5** along peak B', whereas **6** gives **7** (and then **5**) along peak B'_1.

We have also studied the electrochemical behaviour of **5** in the presence of phosphine ligands S′ ($S' = P(CH_3)_2C_6H_5$). Upon addition of S′, wave B is shifted at less negative potential. In cyclic voltammetry peak B' does not appear (Fig. 8). This is consistent with coordination of the phosphine ligand at metallic atom. The reduction of **5** (VLXS′) gives $VLXS'^-$ (**4**), which is very unstable in the presence of S′ and yields VLS'_2 (**6**).

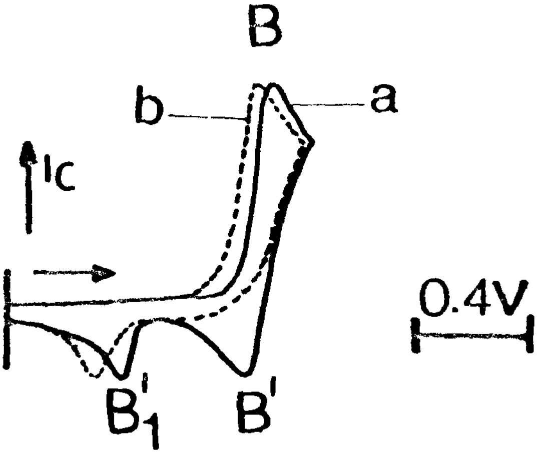


Fig. 8. Cyclic voltammograms of VLXS: starting potential: 0 V; sweep rate 100 mV s^{-1} (a) in thf, (b) in the presence of $P(CH_3)_2C_6H_5$.

We have also studied the voltammogram of chemically prepared **6** in the presence of Cl^- ions. The voltammogram which is obtained is identical with that of Fig. 6. It is also typical of a square scheme reaction, in which **6** gives **7** along peak B'_1. Since there is no peak B', reaction **6** → **4** is too slow to take place at the sweep rate used. As shown by the appearance of peak B (**5** → **4**) on the reverse scan, a small amount of **5** is formed during the oxidation of **6** to **7**.

Square-scheme 2, 3, 4, 5

As shown in Fig. 3a, the reduction of **2** to **3** (peak C_1) is followed by ligand exchange involving replacement of Cl by S to give **4**, which is reoxidized along peak B'. This reaction is relatively slow, since a little **3** is reoxidized directly to **2**, along peak C'_1. A fraction of **4** gives **6**, whose reoxidation peak appears (B'_1).

Experimental

Reagents

The dichlorovanadium(IV) complexes $V^{IV}LCl_2$ and $V^{II}LS_2$ (S = thf) were prepared by published procedures [1,2]. Tetrahydrofuran was purified by distillation from sodium benzophenone ketyl under argon.

The supporting electrolyte was tetrabutylammonium hexafluorophosphate (0.2 *M*) in all cases; the salt (Fluka) was twice recrystallized from ethanol, then dried and deoxygenated before use.

Apparatus and procedure

The electrochemical procedures were carried out under argon at low temperature (−30 °C). The voltammetric experiments were carried out on a platinum disc electrode (Ø: 1.2 mm). For the controlled potential electrolysis, a platinum grid was used. The reference electrode was a saturated calomel electrode separated from the solution by a sintered glass disc. The auxiliary electrode was a platinum wire electrode. A Tacussel UAP 4 Unit connected to a Tektronix oscilloscope (linear potential sweep experiments), a three electrode Tacussel Tipol polarograph, an Amel 552 potentiostat and a Tacussel IG5 integrator were used. The IR spectra were recorded on a Perkin–Elmer model 580B spectrometer.

Characterization of vanadium(III) species

After one-electron reduction of $V^{IV}LX_2$ at -0.8 V (wave A_α) and evaporation of the thf, the complex was extracted with toluene and recrystallized from toluene/heptane (Rdt. 45.5%)). The mass spectrum favours the $V^{III}LX$ formula (m/e 755 ($VLCl^+$), 720 (VL^+)). The molecular weight determined by cryoscopy in benzene was 1551 ($M = 1510$), supporting a dimer formulation.

Far IR spectra in Nujol and in thf show the band expected for vanadium-terminal chloride stretching vibrations (ν(V–Cl) 296 cm^{-1}). Upon addition of thf, this band appears at 305 cm^{-1}, and the other bands are unchanged. Coordination of thf in the V^{III} complex is also consistent with the fact that the one-electron reduction of this complex gives $V^{II}LS_2$, which was also obtained chemically. In the presence of $P(CH_3)_2C_6H_5(S')$, the voltammograms are different, and the one-electro-reduction of $V^{III}LXS'$ gives $V^{II}LS'_2$ which can be obtained chemically [2].

The high-resolution ^1H NMR spectrum in C_6D_6 solution exhibits the resonances observed for diamagnetic porphyrin complexes (protons of p-MeC_6H_4: δ 2.30 (s, 12H, CH_3), 7.05 (m, 8H, *meta* protons), 7.31 (m, 8H, *ortho* protons), and those for protons of the pyrrole rings at δ 8.46 (s, 8H).

All the data are consistent with a mononuclear formulation in a coordinating solvent (thf) and a dimeric arrangement in solvents such as benzene and in the solid state.

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